

# Effect of Fenton-like reactions on the degradation of thiocyanate in water treatment



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## ABSTRACT

Ferric ion ( $\text{Fe}^{3+}$ ) – catalyzed oxidation of thiocyanate by hydrogen peroxide in an aqueous medium was studied. The effects of different parameters such as pH, temperature, catalyst species and the main products of the reaction were identified. The thiocyanate oxidation was found to be efficient if the initial pH of the solution was in the range of 2.5–3.0. The apparent activation energy for the thiocyanate degradation was assessed for different temperatures and determined to be  $37.7 \text{ kJ mol}^{-1}$ . The effects of radical scavengers and air oxygen on the rate of the oxidation of thiocyanate were also studied. The addition of ethanol that acts as a hydroxyl radical scavenger proved the presence of hydroxyl radicals in the  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$  reaction system. The rate of the oxidation of thiocyanate was not dependent on air oxygen. The degradation of thiocyanate was accompanied by the formation of cyanide as the main final product of the reaction. Thus, the catalytic oxidation of thiocyanate makes it possible to return additional NaCN to the production process for leaching of gold and silver.

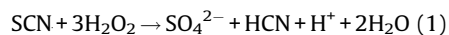
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## 1. Introduction

Cyanide compounds are widely used in gold ore processing plants in order to facilitate the extraction and subsequent concentration of the precious metals. Owing to the high cyanide concentrations employed for the extraction of gold or silver from sulfide ores or concentrates, effluents generated have high contents of cyanide and thiocyanate, which lend them a high degree of toxicity [1–7]. The cyanide reacts with both sulfide minerals and partially oxidized sulfur intermediates to produce thiocyanate [3,5,7]. The formation of thiocyanate is an undesired side reaction and in many cases, thiocyanate formation results in prohibitively high cyanide consumption and has a negative influence for the sorption process of gold [6]. Because thiocyanate is not destroyed in most cyanide detoxification processes, an additional treatment technology for thiocyanate removal is necessary [7].

Different degradation techniques have been proposed for the treatment of these kinds of streams. The biological treatment is one of the most reliable and most economical options but its application range is limited to low pollutant concentrations and

also gives inhibitory effects in microorganism activity [8,9]. Electrochemical processes are inefficient after thiocyanate falls below a certain level; requiring higher currents. The most commonly used method for removal of  $\text{SCN}^-$  in wastewater is the direct alkaline chlorination or the addition of hypochlorite. This method has disadvantages such as chloride contamination and involvement of reactants that are hazardous and unsafe to handle [10]. Hydrogen peroxide, an environmentally friendly oxidant, can be proposed as an alternative to chlorine. The use of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is the basis of one of the most effective methods for cyanide and thiocyanate destruction. Hydrogen peroxide is easy to handle, it does not form insoluble salts (which create their own waste disposal problems) and the residual hydrogen peroxide degrades to water and oxygen. Moreover, at low pH, hydrogen peroxide is capable of oxidizing thiocyanate to cyanide via the Reaction (1)[11,12]:



This process is able to recover cyanide from thiocyanate to reduce tailings toxicity and to allow the reuse of cyanide otherwise lost to thiocyanate formation. Cyanide recoveries pointed to the fact that if a method for reutilization of cyanide contained in mining effluents is employed, precious metal processing will become more efficient. Also, the environmental conditions in the area of the operation will be improved [5,7,13,14].

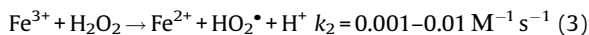
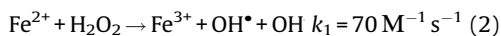
The direct oxidation of  $\text{SCN}^-$  by hydrogen peroxide proceeds rather slowly. To accelerate production of HCN a catalyst should

Abbreviations: C, concentration of component in the reaction mixture;  $C_0$ , initial concentration of component in the reaction mixture;  $E^0$ , oxidation potential; k, reaction rate constant; w, reaction rate; T, temperature;  $E_a$ , apparent activation energy; R, ideal gas constant; A, pre-exponential factor.

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to be added into the reactive mixture. It is known that the non-selective and highly oxidative hydroxyl radicals are formed in the presence of hydrogen peroxide and ferrous or ferric salts. The process is based on electron transfer reactions between hydrogen peroxide and ferrous ions ( $\text{Fe}^{2+}$ ), the combination of which makes what is called Fenton's reagent. When the catalyst is other than  $\text{Fe}^{2+}$  (e.g., ferric ions ( $\text{Fe}^{3+}$ )), the reaction proceeds similarly but is known as the Fenton-like process. The Fenton and Fenton-like systems can be described by the following reactions [15–17]:



The oxidation processes which generate hydroxyl radicals ( $E^0 = 2.8 \text{ eV}$ ) in sufficient quantity are defined as advanced oxidation processes (AOPs), which are very effective in oxidizing both organic and inorganic pollutants. Most of the AOPs use a combination of strong oxidants like  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  with catalysts like transition metals, iron, semiconductor solids, and radiation or ultrasound [18]. Among AOPs, Fenton and Fenton-like processes are cost-effective, easy to apply and effective methods of treating effluents containing a wide range of contaminants. One of the advantages of the Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cost effective source of hydroxyl radicals, using easy-to-handle reagents. On the other hand, the generation of Fe-containing sludge is the main disadvantage in Fenton-like treatment [19].

In spite of numerous studies of the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  system, the chemistry and kinetics of the oxidation of different contaminants by Fenton-like processes ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system) have not been well elucidated [17]. Moreover, in the open literature there are no reports about the applicability of Fenton-like process as well as Fenton process for the degradation of recalcitrant inorganic contaminants, such as thiocyanate, in effluents.

The aim of the research was the investigation of the main regularities of catalytic oxidation of thiocyanate by environmentally friendly oxidants in order to determine the effect of different parameters on the oxidation efficiency and the possibility of regeneration of cyanide from thiocyanate.

## 2. Materials and methods

### 2.1. Chemicals

A standard solution of thiocyanate was prepared by dissolving analytical grade potassium thiocyanate salt in distilled water. The starting concentrations of thiocyanate were 1.72 and  $17.2 \text{ mmol L}^{-1}$  according to the typical concentrations of thiocyanate containing wastewater and the initial pH was adjusted to 3.0 with  $3.0 \text{ mol L}^{-1}$  hydrochloric acid. In all processes, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was used as the oxidant. Copper (II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and iron (II) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were used as catalysts. All experiments were carried out using solutions prepared from analytical grade reagents and distilled water.

### 2.2. Procedures and analytical methods

Three replicates of each experiment were carried out. The data reproducibility was better than  $\pm 10\%$  in all the cases. All

experiments were performed at ambient pressure within the range of  $15\text{--}50^\circ\text{C}$  in a 250 mL glass vessel using a total volume of 200 mL under constant stirring with a magnetic stir bar, and temperature control. During the experiments, a number of samples were removed at predetermined intervals to monitor the concentration of thiocyanate and cyanide. Immediately after sampling, sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) was added to the samples for quenching of oxidation reaction. The concentration of thiocyanate was measured using a spectrophotometric method, which involves the reaction of thiocyanate with ferric iron to produce a series of colored complexes with an absorption maximum at 460 nm [20]. The cyanide was measured using the spectrophotometric determination by the pyridine–barbituric acid method [21], concentration of sulfate was determined by the titrimetric method [22]. The strength of the hydrogen peroxide solution was determined by a standard method using potassium permanganate [23]. The pH was also monitored during the experiments.

For the process under study a gas washing bottle or Drechsel bottle provides an effective method for extraction of HCN formed during  $\text{SCN}^-$  oxidation. Following oxidation of the thiocyanate, free cyanides are converted to hydrogen cyanide. The liberated hydrogen cyanide is purged with oxygen of air into an alkaline "trap" containing an absorbing solution of sodium hydroxide. The cyanide concentration in the alkaline solution is determined by colorimetric detection.

## 3. Results and discussion

The amount of reagents is the most important control variable in Fenton-like oxidation reactions. To select the optimum concentrations of the ferric ion and hydrogen peroxide, experiments were run using an aqueous solution of  $17.2 \text{ mmol L}^{-1}$  of thiocyanate. The results showed that under the specified conditions, maximum effects were observed at  $\text{Fe}^{3+} = 3.6$  and  $51.6 \text{ mmol L}^{-1}$  of hydrogen peroxide. It was found that the optimum molar ratio of  $[\text{SCN}^-]:[\text{H}_2\text{O}_2]:[\text{Fe}^{3+}]$  was 3:1:0.2 [24]. This is in agreement with the stoichiometric balance Eq. (1) in which 3 mol of  $\text{H}_2\text{O}_2$  is sufficient for 1 mol of  $\text{SCN}^-$ .

### 3.1. Preliminary catalysts test

A set of homogeneous transition metal salts has been tested as catalysts for the thiocyanate degradation (Fig. 1). As can be seen, copper (II) scarcely changed the rate of thiocyanate degradation.

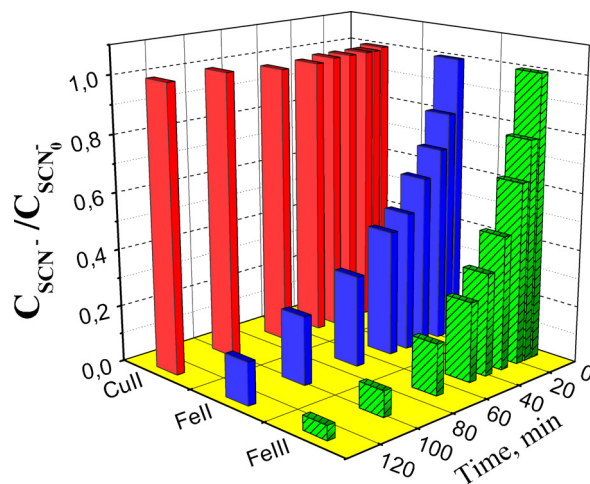


Fig. 1. Degradation of thiocyanate concentration during oxidation carried out in the presence of different metals: copper(II), iron (II) and iron (III).  $[\text{SCN}^-] = 1.72 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 5.16 \text{ mmol L}^{-1}$ ;  $[\text{Me}] = 0.36 \text{ mmol L}^{-1}$ ; pH 3.0.

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